

Article

Genetic Mechanisms of Geothermal Resources in the Middle Segment of the Yishu Fault Zone (China): Insights from Hydrochemistry and Multi-Isotopes (δD , $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $\delta^{34}S$) Analysis

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Abstract

The Yishu Fault Zone (YSFZ) is located in a key tectonic transition zone shaped by the interaction between the Pacific and Tethyan tectonic domains in eastern China. Despite sparse geothermal borehole coverage across this region, the deeply incised fault structures create favorable hydrogeological prerequisites for fault-mediated subsurface heat migration and hydrothermal fluid circulation. This study integrates hydrochemistry, multi-isotope tracing (δD , $\delta^{18}O$, $^{87}Sr/^{86}Sr$, and $\delta^{34}S$), multi-mineral equilibrium modeling, and silica–enthalpy mixing analysis to constrain the evolution process and genetic mechanism of geothermal groundwater in the middle segment of the YSFZ. The geothermal groundwater displays weakly alkaline to alkaline properties and in situ temperatures of 35.2–75.0 °C, which is characterized by the HCO_3^-Na , SO_4-Na , and $Cl\cdot SO_4-Na$ type. Stable isotope signatures demonstrate that the geothermal groundwater is recharged by the atmospheric precipitation with elevations of 822–1274 m. The hydrochemical evolution of the geothermal waters is governed by silicate weathering, evaporite dissolution, and cation exchange. The $^{87}Sr/^{86}Sr$ ratios indicate mixed solute contributions from silicate and evaporite lithologies, whereas the $\delta^{34}S$ signatures suggest that SO_4^{2-} is predominantly derived from gypsum dissolution. Two distinct hydrochemical evolution patterns can be identified in the study area. Samples GG1 and GG5 are characterized by HCO_3^- enrichment, whereas GG2, GG3, and GG4 exhibit enrichment in Na^+ and SO_4^{2-} . Reservoir temperatures estimated using multi-mineral equilibrium geothermometry range from 56.7 °C to 92.1 °C, with circulation depths of 1648–2304 m and cold-water mixing ratios of 48%–69%. The results of this study provide geochemical evidence for hidden geothermal resource exploration in deep fault zones.



Academic Editor: Liliana Lefticariu

Received: 27 May 2026

Revised: 1 July 2026

Accepted: 6 July 2026

Published: 10 July 2026

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Keywords: geothermal groundwater; hydrochemistry; multi-isotopes (D; O; S; and Sr); reservoir temperature; the Yishu Fault

1. Introduction

Geothermal energy, characterized by a stable heat supply and relatively low environmental impact, has become an important component of low-carbon energy systems [1,2]. Among various geothermal resources, fault-controlled medium-temperature

to low-temperature geothermal systems are widely distributed in continental tectonically active regions and are of great significance for regional geothermal exploration and development [3]. Deep-seated faults and their associated fracture networks not only provide preferential pathways for meteoric water infiltration, deep circulation, and thermal fluid upwelling, but also control deep heat transfer, water–rock interaction, and the hydrochemical evolution of geothermal waters [4]. Therefore, the formation of fault-controlled geothermal systems is commonly governed by multiple factors, including fault architecture, heat source conditions, reservoir lithology, and water–rock interaction. Hydrochemical and isotopic methods are indispensable tools for revealing the genetic mechanisms of such geothermal systems. Ions ratio relationship delineates hydrochemical facies and dominant water–rock interaction processes [5]; δD and $\delta^{18}O$ identify recharge sources and recharge elevations [6]; $^{87}Sr/^{86}Sr$ indicate solute sources and the intensity of water–rock interaction [7]; and $\delta^{34}S$ distinguishes sulfate sources [8]. Integrating geochemical geothermometers, multi-mineral equilibrium simulations, and silica–enthalpy mixing models enables the systematic quantification of reservoir temperature, circulation depth, and cold-water mixing ratios. This combined method provides robust integrated constraints for the characterization and interpretation of buried geothermal systems.

As the middle segment of the Tanlu Fault Zone, the Yishu Fault Zone (YSFZ) represents a critical lithospheric deep fault in eastern China. Tectonically, this zone is situated within a transitional domain controlled by the interplay between the Pacific and Tethyan tectonic systems and adjacent to the boundary of the North China Craton and Yangtze Craton [9]. Long-term tectonic activation, magmatic intrusion, metamorphism, and fault reactivation collectively generate favorable geological conditions for geothermal anomalies. Owing to its deeply incised fault structures, the YSFZ enables upward deep heat migration and subsurface fluid circulation, rendering it a typical site for exploring fluid circulation, heat transport, and geothermal formation within intracontinental deep faults. Nevertheless, distinct from well-developed hydrothermal fields, the YSFZ middle segment is characterized by sparse borehole coverage and weak surface hydrothermal manifestations. Previous studies regarding YSFZ geothermal systems are confined to regional geological surveys and single-borehole hydrochemical analyses, lacking quantitative constraints on recharge mechanisms, water–rock interactions, solute provenances, thermal reservoir conditions, and mixing dynamics. Given the scarcity of hydrothermal outcrops, individual geochemical approaches fail to decipher subsurface genetic mechanisms. Accordingly, integrated hydrochemical, multi-isotope, and thermodynamic methods are essential to constrain the geothermal evolution. Multiple isotopes (δD , δO , $^{87}Sr/^{86}Sr$, and δS) provide sufficient evidence for recharge sources and lithological controls, while multi-mineral equilibrium and silica–enthalpy models further reconstruct the complete circulation evolution of geothermal fluids.

This study analyzes the genetic mechanism of geothermal groundwater in the middle segment of the Yishu Fault Zone through hydrochemical and isotopic methods. (1) The hydrochemical analysis is employed to characterize the major ion composition and dominant controlling processes. (2) A multi-isotope approach (δD , $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $\delta^{34}S$) is utilized to elucidate the fluid origin and calculate the recharge elevation. (3) Estimating the reservoir temperature. Silica geothermometers and mineral equilibrium simulations are applied, followed by a quantitative assessment of the circulation depth and cold-water mixing ratio. (4) Constructing a conceptual model. The integrated results are synthesized to establish a coherent circulation model that clarifies the overall formation mechanism of the geothermal system. The results provide geochemical evidence for understanding the genesis of fault-controlled medium–low temperature geothermal systems and offer

scientific support for the exploration of concealed geothermal resources in the YSFZ and similar deep fault zones.

2. Geological Setting

The Yishu Fault Zone (YSFZ) is the dominant regional structural system in the study area and has been tectonically active since the Late Pleistocene. It trends NNE ($10\text{--}25^\circ$), extending for approximately 330 km with a width of 20–60 km. The fault zone converges southward and bifurcates northward [10]. It comprises four major fault systems, namely the Changyi–Dadian Fault, Anqiu–Juxian Fault, Yishui–Tangtou Fault, and Tangwu–Gegou Fault (Figure 1) [11], each consisting of multiple subparallel fault strands. These faults are deep-seated structures that cut through the crust and extend into the upper mantle. Their interaction has produced a characteristic two-graben–one-horst configuration in the central segment, while the northern and southern termini correspond to Mesozoic–Cenozoic basinal depression [12]. Owing to its deep penetration and strong structural segmentation, the YSFZ serves as a major conduit for deep fluid migration and heat transport.

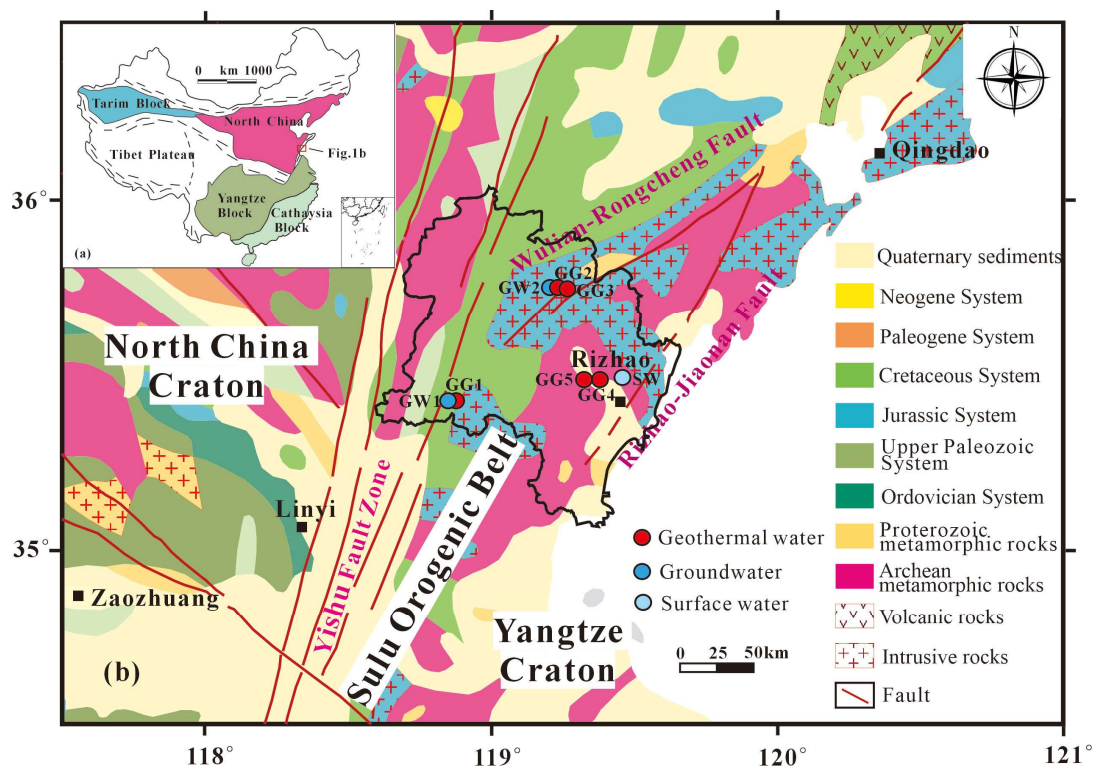


Figure 1. (a) Tectonic map of the major tectonic divisions of China; (b) Simplified geological map and distribution of sampling locations in the study area (modified after Li et al. [11]).

The study area lies at the junction between the Ludong Uplift and the YSFZ, within the central segment of the Sulu ultra-high-pressure (UHP) metamorphic belt at the boundary between the North China and Yangtze plates (Figure 1). The Indosinian collision between these two plates produced widespread UHP metamorphism, whereas subsequent Yanshanian granitic intrusions significantly reworked the regional thermal structure and elevated geothermal gradients. In addition, prolonged subduction of the Paleo-Pacific Plate during the Mesozoic–Cenozoic further influenced the tectono-thermal evolution and magmatic activity of eastern China [13,14]. Collectively, these processes resulted in a complex tectonic overprint and enhanced regional geothermal anomalies.

The lithological framework of the study area is composed mainly of Precambrian crystalline basement, Paleozoic carbonate–clastic strata, Mesozoic–Cenozoic volcanic–

sedimentary successions, and Yanshanian intrusive rocks [15,16]. The Precambrian basement in and around the YSFZ includes the Mesoarchean Yishui Group, Neoarchean Taishan Group, and Neoproterozoic Tumen Group. The Yishui Group is mainly composed of granulite and amphibolite with minor quartzite, whereas the Taishan Group consists predominantly of amphibolite, biotite granulite, and minor TTG gneiss [12]. The Tumen Group is characterized by shale, sandstone, limestone, and conglomerate. These basement rocks are locally overlain by Paleozoic fluvial clastic rocks, marine clastic rocks, and carbonate rock. The overlying Mesozoic–Cenozoic strata are dominated by volcano-sedimentary rocks developed in fault-controlled basins. In particular, the Cretaceous Qingshan Group mainly consists of intermediate to felsic continental volcanic rocks, whereas the Dasheng and Wangshi groups are composed chiefly of continental lacustrine clastic and volcanic rocks [17]. In addition, Yanshanian granitic intrusions and associated volcanic rocks are widely developed and have significantly reworked the regional thermal structure. The coexistence of metamorphic basement, carbonate–clastic cover, volcanic–sedimentary rocks, granitic intrusions, and deep-reaching faults provides favorable geological conditions for heat accumulation, fracture-controlled groundwater circulation, and active water–rock interaction [15]. Although no active magma chamber has been identified beneath the study area, residual magmatic heat, crustal heat flow, and deep fault-controlled heat transfer may jointly contribute to the present-day geothermal regime.

Based on groundwater occurrence, burial depth, and hydraulic connectivity, groundwater in the study area can be classified into three types: pore water in unconsolidated sediments, pore–fissure water in clastic rocks, and bedrock fissure water. Pore water in unconsolidated sediments is mainly distributed in Quaternary deposits in valleys and plains, characterized by shallow burial depth and strong hydraulic connectivity. Pore–fissure water in clastic rocks occurs primarily within Cretaceous sedimentary strata and is controlled by both primary porosity and secondary fractures. Bedrock fissure water is hosted in metamorphic and granitic rocks and predominantly circulates along fault and fracture networks. Overall, groundwater flow is primarily governed by topographic gradients, moving from upland recharge zones toward downstream valleys.

3. Sampling and Analytical Methods

3.1. Sample Collection and Measuring

In this study, a total of 5 samples were collected from the study area (Figure 1), including 2 geothermal samples (GG1, GG2), 2 groundwater samples (GW1, GW2), and 1 surface water sample (SW). Three sets of geothermal groundwater data, namely GG3, GG4, and GG5, are collected from the literature [18]. Owing to the concealed occurrence of geothermal resources and the limited number of accessible geothermal wells in the middle segment of the Yishu Fault Zone, the number of geothermal water samples available for this study is relatively limited. The pH, electrical conductivity (EC), and total dissolved solids (TDSs) are measured on-site using calibrated portable multi-parameter water quality detectors (SX-620, SX-630, and SX-650; Shanghai Sanxin Instrument Factory, Shanghai, China). Water temperature (T) and dissolved oxygen are measured using a handheld multi-parameter meter (HQ40D, Hach Company, Loveland, CO, USA).

At each site, three types of samples are obtained, including a 500 mL sample for major cations and anions, a 200 mL sample for hydrogen and oxygen isotopes, and a 200 mL sample for strontium and sulfur isotopes. Water samples are filtered through a 0.45 µm micron membrane and stored in high-density polyethylene (HDPE) bottles, which are rinsed three times with the water samples. Every bottle is sealed with sealing film to prevent leakage and evaporation before being sent to the laboratory for testing. After collection, all samples are stored in a cool and dark place to avoid direct sunlight and

delivered to the laboratory for testing within three days. Laboratory testing of cations and anions is completed at Guirui Testing Technology (Beijing) Co., Ltd., (Beijing, China) mainly including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , and SO_4^{2-} , which are determined by ion chromatography (Shimadzu LC-10ADvp, Shimadzu Corporation, Kyoto, Japan), and the HCO_3^- concentration is determined by titration using a HACH digital titrator (Hach Company, Loveland, CO, USA). $\delta^{18}O$ and δ^2H are measured using a liquid water isotope analyzer (LGR, DLT-100, Los Gatos Research, Mountain View, CA, USA) according to the Vienna Standard Mean Ocean Water (VSMOW). Sr and S isotopes are measured using a Phoenix thermal surface ionization mass spectrometer (Isotopx Ltd., Middlewich, Cheshire, UK) and a Delta V Advantage stable isotope mass spectrometer (Thermo Fisher Scientific (Bremen) GmbH, Bremen, Germany) at the Institute of Geographic Sciences and Natural Resources, Chinese Academy of Sciences.

3.2. Reservoir Temperature Estimation Methods

Reservoir temperature estimation is performed using geochemical geothermometry and mineral equilibrium calculations. The measured field parameters, including temperature and pH, together with the analytical concentrations of major ions and dissolved silica, are used as input data.

The water–rock equilibrium state is first evaluated using the Na–K–Mg ternary diagram. The concentrations of Na^+ , K^+ , and Mg^{2+} are converted to the required plotting parameters of $Na/1000$, $K/100$, and $SQRT(Mg)$, respectively. The position of each geothermal water sample in the diagram is used to classify the water as immature, partially equilibrated, or equilibrated.

Mineral saturation indices are calculated to evaluate the equilibrium state between geothermal water and selected reservoir minerals. The saturation index is calculated using the following equation:

$$SI = \log(Q/K) \quad (1)$$

where Q is the ion activity product and K is the thermodynamic equilibrium constant of the corresponding mineral reaction. An SI value of 0 indicates mineral equilibrium, $SI > 0$ indicates supersaturation, and $SI < 0$ indicates undersaturation. In this study, minerals with SI values ranging from -0.5 to 0.5 are considered to be close to equilibrium. The selected minerals include anhydrite, aragonite, calcite, chalcedony, dolomite, fluorite, gypsum, and quartz.

The multi-mineral equilibrium method is used to estimate reservoir temperature. The variation in mineral saturation indices with temperature is calculated using the GeoT program and the SOLTHERM.H06 thermodynamic database. For each geothermal water sample, SI -temperature curves of the selected minerals are generated, and the reservoir temperature is determined from the temperature interval where multiple mineral curves converged near $SI = 0$.

Classical silica geothermometers are also applied for comparison. The reservoir temperatures are calculated using quartz, chalcedony, α -quartz, β -quartz, and amorphous silica geothermometers. The calculated results are then compared with the temperatures obtained from the multi-mineral equilibrium method.

4. Results

4.1. Hydrochemical Characteristic

Table 1 presents the physicochemical parameters and chemical compositions of the collected samples in the study area. The pH value ranges from 7.72 to 8.80, indicating a weakly alkaline to alkaline environment, whereas that of groundwater ranges from 6.84 to 7.16, reflecting essentially neutral conditions. The pH of surface water is 7.51, indicating

weak alkalinity. The TDSs of geothermal water range from $285 \text{ mg}\cdot\text{L}^{-1}$ to $1495 \text{ mg}\cdot\text{L}^{-1}$, while the TDSs of surface water are $242 \text{ mg}\cdot\text{L}^{-1}$, and that of groundwater ranges from $294 \text{ mg}\cdot\text{L}^{-1}$ to $428 \text{ mg}\cdot\text{L}^{-1}$.

Table 1. Hydrochemical parameters of water samples from the study area.

Sample ID	Water Sample Type	Temperature (°C)	pH	TDS (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl [−] (mg/L)	SO ₄ ^{2−} (mg/L)	HCO ₃ [−] (mg/L)	CO ₃ ^{2−} (mg/L)	H ₂ SiO ₃ (mg/L)
GG1	Geothermal water	35.2	8.24	471	2.77	0.33	182.0	1.26	73.30	83.40	244.0	11.90	23.40
GG2	Geothermal water	-	7.72	1036	43.70	0.10	320.0	17.40	191.00	740.00	51.2	<0.50	64.10
GG3	Geothermal water	75.0	8.70	1495	92.58	0.55	369.9	15.28	206.20	655.25	48.3	11.88	145.73
GG4	Geothermal water	37.0	8.00	750	45.29	0.95	206.5	3.25	132.24	322.28	61.9	0	24.56
GG5	Geothermal water	40.0	8.80	285	2.57	0.15	104.6	0.88	25.88	48.99	144.4	11.59	22.02
GW1	Groundwater	15.8	6.84	428	68.90	52.40	59.3	2.37	47.00	106.00	276.0	<0.50	41.00
GW2	Groundwater	16.9	7.16	294	51.40	22.30	31.8	2.91	27.10	70.10	169.0	<0.50	29.80
SW	Surface water	11.2	7.51	242	21.70	11.20	15.1	3.26	10.40	28.50	79.6	<0.50	18.70

Note: when the pH exceeds 8, the carbonate equilibrium system shifts toward deprotonation, allowing a portion of HCO_3^- to convert into CO_3^{2-} ; consequently, small amounts of CO_3^{2-} can be detected in the water.

For cations, Na^+ dominates the cations in geothermal water, while Ca^{2+} dominates the cations in surface water and groundwater. In geothermal groundwater, the abundance of cations from high to low is Na^+ , Ca^{2+} , K^+ and Mg^{2+} , while in groundwater and surface water, Ca^{2+} content is the highest, followed by Na^+ and Mg^{2+} , and, finally, K^+ . The rock layer through which groundwater passes is mainly andesite. The main mineral components of andesite are hornblende and feldspar, which contain high contents of sodium, potassium and calcium ions. At the same time, the movement of groundwater is in a high temperature and high pressure environment, which is conducive to the precipitation of sodium, potassium and calcium ions. The long runoff time is also conducive to the accumulation of ions, which gradually increases the sodium, potassium and calcium ions in underground hot water [19].

As for anions, HCO_3^- is the dominant anion in surface water and groundwater, while HCO_3^- and SO_4^{2-} are the dominant anions in geothermal water. SO_4^{2-} occupies a dominant position among anions in geothermal water, mainly because surface water infiltrates at the intersection of fractures and brings in atmospheric oxygen. When it circulates to the heat storage area, atmospheric oxygen acts as an oxidant in the process of S^{2-} generating SO_4^{2-} , generating SO_4^{2-} , so that SO_4^{2-} is relatively enriched [20]. In groundwater and surface water, HCO_3^- content is the highest, followed by SO_4^{2-} and, finally, Cl^- .

Based on the Pearson correlation coefficient matrix (Figure 2), the ions in the geothermal water system in the study area show significant correlation characteristics. Na^+ and Cl^- exhibit an extremely strong positive correlation ($r = 0.97$); Ca^{2+} and SO_4^{2-} show a very weak positive correlation ($r = 0.17$), while Ca^{2+} and HCO_3^- display a very weak positive correlation ($r = 0.14$). Na^+ and SO_4^{2-} present a strong positive correlation ($r = 0.88$), and Mg^{2+} and HCO_3^- show a moderate positive correlation ($r = 0.59$). For combined ion pairs, Na^+ and $\text{Cl}^- + \text{SO}_4^{2-}$ show an extremely strong positive correlation.

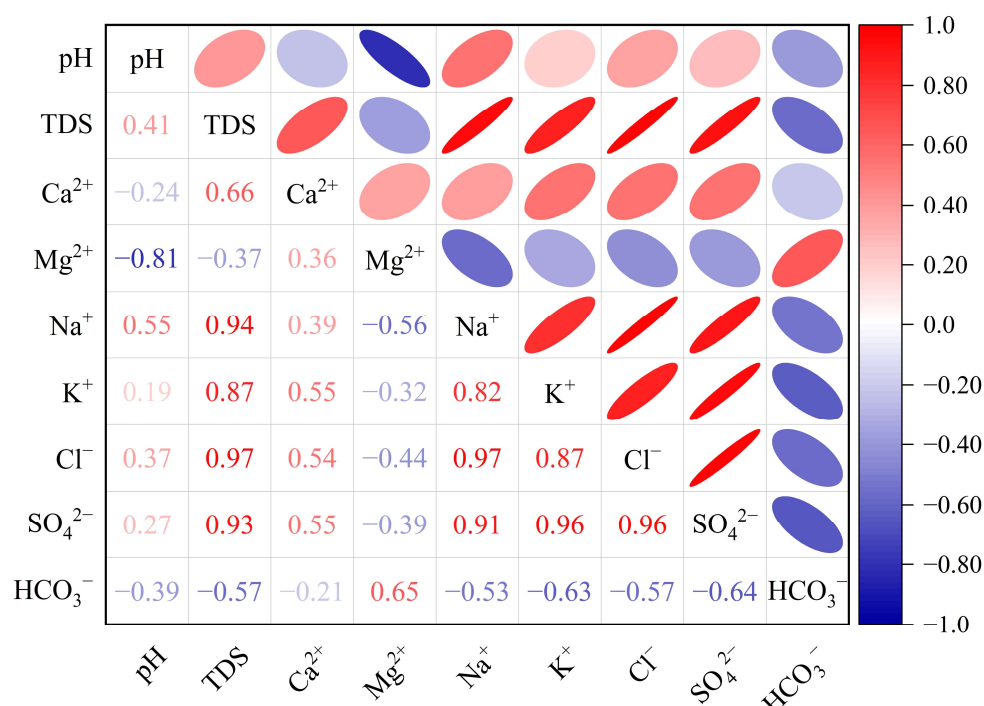


Figure 2. Pearson correlation analysis of physicochemical parameters in geothermal water samples from the study area.

The Piper diagram is a classic hydrogeochemical tool for classifying water chemical type [21]. Figure 3 shows obvious compositional differences among various water bodies. Geothermal water (GG1~GG5), surface water (SW) and groundwater (GW1, GW2) have different hydrochemical types. The geothermal waters exhibit a distinct hydrochemical facie. GG1 and GG5 are of the HCO₃-Na type, GG2 is characterized by the SO₄-Na type, and GG3 and GG4 are classified as Cl·SO₄-Na type. In contrast, surface water and groundwater GW1 share an HCO₃·SO₄-Na·Ca·Mg signature, while groundwater GW2 is characterized as an HCO₃·SO₄-Ca·Mg type.

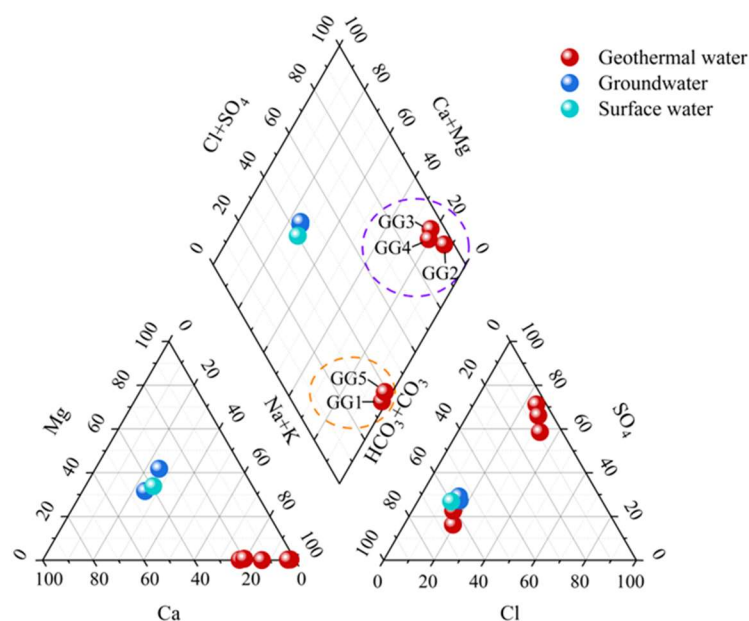


Figure 3. Piper diagram illustrating the hydrochemical facies of geothermal water, groundwater, and surface water samples from the study area.

4.2. Isotopic Characteristic

The isotopic characteristics of geothermal water, groundwater, and surface water in the study area are shown in Table 2. The δD values for geothermal and non-geothermal water are -72.0‰ to -67.2‰ , averaging -69.2‰ and -53.6‰ to -52.3‰ , averaging -53.1‰ , respectively; the $\delta^{18}O$ values are -10.0‰ to -9.4‰ , averaging -9.7‰ and -8.0‰ to -7.2‰ , averaging -7.7‰ , respectively. Among the geothermal water samples, $^{87}Sr/^{86}Sr$ data are available only for GG1 and GG2, with values of 0.7095 and 0.7105, respectively. For the non-geothermal waters, the $^{87}Sr/^{86}Sr$ ratios range from 0.7103 to 0.7110. The $^{87}Sr/^{86}Sr$ data of GG3, GG4, and GG5 are not reported in the original literature. For sulfur isotopes, $\delta^{34}S$ data are available only for GG1 and GG2 among the geothermal water samples, with values of 24.5‰ and 12.8‰, respectively. The $\delta^{34}S$ values of groundwater samples range from 3.9‰ to 8.4‰, and that of the surface water sample is 5.0‰. For GG3, GG4, and GG5, $\delta^{34}S$ data are not reported in the original literature.

Table 2. Isotopic composition of water samples from the study area.

Sample ID	$\delta D\text{‰}$	$\delta^{18}O\text{‰}$	$^{87}Sr/^{86}Sr$	$\delta^{34}S\text{‰}$
GG1	−67.2	−9.4	0.7095	24.5
GG2	−68.8	−10.0	0.7105	12.8
GG3	−69.0	−9.5	n.d.	n.d.
GG4	−69.0	−9.6	n.d.	n.d.
GG5	−72.0	−10.0	n.d.	n.d.
GW1	−53.6	−8.0	0.7103	8.4
GW2	−52.3	−7.8	0.7110	3.9
SW	−53.3	−7.2	0.7106	5.0

Note: n.d. indicates not determined. The hydrochemical data of GG3, GG4, and GG5 are collected from the published literature, in which $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ data are not reported.

5. Discussion

5.1. Origin of Geothermal Water

5.1.1. Recharge Sources

Hydrogen and oxygen isotopes are important tools for identifying the recharge source of groundwater. As is shown in Figure 4, the hydrogen and oxygen isotope values of collected samples are distributed along the global atmospheric precipitation line (GMWL) and the local atmospheric precipitation line (LMWL) [22]. The absence of significant oxygen-isotope drift suggests that geothermal water, groundwater, and surface water in the study area share a common recharge source derived from atmospheric precipitation.

5.1.2. Recharge Elevation

The hydrogen and oxygen isotopes of atmospheric precipitation exhibit an elevation effect, meaning that the δD (or $\delta^{18}O$) value decreases with increasing elevation [23]. This characteristic can be used to estimate the recharge elevation:

$$H = \frac{\delta_G - \delta_P}{K} + h \quad (2)$$

where H is the recharge elevation (m); h is the sampling point elevation (m); δ_G is the δD (or $\delta^{18}O$) value of the sampled water; δ_P is the δD (or $\delta^{18}O$) value of the atmospheric precipitation near the sampling point; and K is the isotope elevation gradient (‰ per 100 m). The δD and $\delta^{18}O$ values of atmospheric precipitation are used as reference values, with altitude gradients of $-3.0\text{‰}/100\text{ m}$ for δD and $-0.58\text{‰}/100\text{ m}$ for $\delta^{18}O$ [24].

Based on the average values, the calculated recharge elevations for GG1 and GG2 are 674 m and 833 m, respectively. However, the ascent of geothermal water is affected

by mixing with shallow cold water to varying degrees, leading to elevated measured δD and $\delta^{18}O$ values in the geothermal water and, consequently, resulting in underestimated recharge elevations. Therefore, it is necessary to correct the δD and $\delta^{18}O$ values of the geothermal water. For this purpose, a binary mixing model is introduced to reconstruct the original oxygen isotopic composition of the geothermal water (Equation (3)).

$$A \times (1 - X) + B \times X = C \quad (3)$$

where X represents the mixing ratio of cold water in the mixed geothermal water; A and B denote the isotopic ratios of the original (unmixed) geothermal water and the non-thermal end member, respectively; and C represents the measured isotopic ratio of the mixed geothermal water (sample).

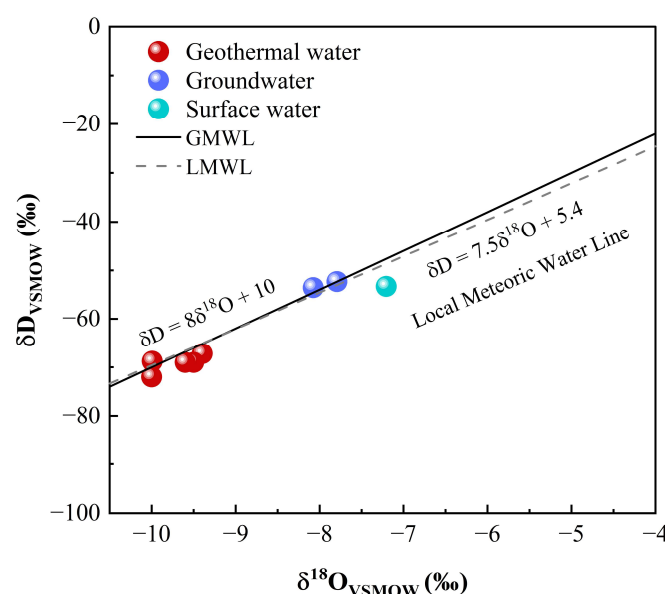


Figure 4. δD - $\delta^{18}O$ relationships of geothermal water, groundwater, and surface water in the study area, plotted alongside the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL).

The $\delta^{18}O$ value of non-thermal water ($-8.0‰$) is used as the shallow cold-water end member, and the cold-water mixing proportions are taken from the silicon–enthalpy model. After correction, the $\delta^{18}O$ values of GG1 and GG2 are $-10.4‰$ and $-12.8‰$, respectively, corresponding to corrected recharge elevations of 822 m and 1274 m. Thus, the recharge elevation range of 822–1274 m refers only to GG1 and GG2. Because GG3, GG4, and GG5 are collected from the published literature and their original sampling elevations are not available, recharge elevation correction is not performed for these samples.

5.2. Hydrochemical Processes

The Gibbs diagram is an important tool for identifying the source and control mechanism of water ions in hydrochemistry. Using the relationship diagram between TDSs and $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$, the genesis types of groundwater hydrochemical components can be divided into three categories: evaporation concentration type, rock weathering type, and precipitation control type. The Gibbs diagram can be used to qualitatively analyze the factors affecting the hydrochemical components and determine the source of each ion element in the water body [25]. As shown in Figure 5, geothermal water cation data points are mainly concentrated on the right side of the Gibbs diagram (where the horizontal axis value exceeds 0.5), indicating that their composition is influenced

not only by water–rock interaction but also by cation exchange and human activities [26]. Geothermal water anion data points are distributed on both sides of the diagram: specifically, the points on the left (GG1, GG5) indicate that water–rock interaction is the primary controlling mechanism of geothermal water chemistry in the region, while the points on the right (GG2, GG3 and GG4) reflect the combined effects of water–rock interaction, cation exchange, and human activities. Surface water and groundwater composition changes are mainly controlled by rock weathering.

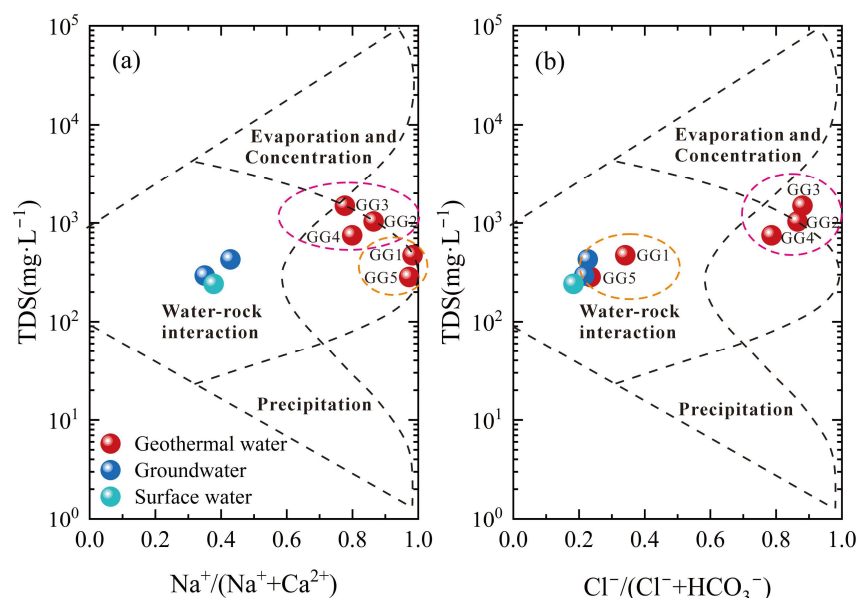


Figure 5. (a) Gibbs diagram showing TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ for the waters; (b) Gibbs diagram showing TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$. The diagrams illustrate the controlling mechanisms of hydrochemical composition in geothermal water, groundwater, and surface water from the study area.

$^{87}\text{Sr}/^{86}\text{Sr}$ do not fractionate during mineral weathering, and water bodies formed in different lithologies may exhibit different Sr isotopic characteristics. They have been widely used in hydrogeochemical studies, often to trace the source of dissolved strontium in groundwater and assess the extent of water–rock interaction [2,27]. In this study, $^{87}\text{Sr}/^{86}\text{Sr}$ data are available for GG1 and GG2 among the geothermal water samples, with values of 0.7095 and 0.7105, respectively, whereas GG3, GG4, and GG5 are not included in the Sr isotope interpretation because their $^{87}\text{Sr}/^{86}\text{Sr}$ data are not reported in the original literature. The available $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all analyzed water samples range from 0.7095 to 0.7110 (Figure 6), indicating mixed Sr contributions from multiple lithological sources. Relatively low to moderate $^{87}\text{Sr}/^{86}\text{Sr}$ values may be related to carbonate and evaporite mineral dissolution, whereas relatively higher $^{87}\text{Sr}/^{86}\text{Sr}$ values may reflect interaction with radiogenic silicate rocks, granitic rocks, and metamorphic basement rocks in the upper crust [27]. Combined with Sr concentrations ranging from 0.18 to 4.40 mg/L, these results suggest that the dissolved Sr in the geothermal waters is controlled by mixed water–rock interaction involving carbonate, evaporite, silicate and metamorphic lithologies.

Binary plots of the $\text{Ca}^{2+}/\text{Na}^+$ molar ratio, the $\text{Mg}^{2+}/\text{Na}^+$ molar ratio, and the $\text{HCO}_3^-/\text{Na}^+$ molar ratio are used to distinguish evaporite dissolution, carbonate dissolution, and silicate dissolution processes [28,29]. Figure 7a shows that all geothermal water samples are distributed near the evaporite end member. Figure 7b shows that samples GG1 and GG5 are distributed near both the evaporite and silicate end members, while samples GG2, GG3, and GG4 are distributed near the evaporite end member. This indicates that the hydrochemical composition of the geothermal waters in the study area is primarily controlled by evaporite dissolution. In addition, surface water and groundwater

samples are distributed near the silicate end member, indicating that the hydrochemical composition of surface water and groundwater in the study area is primarily controlled by silicate dissolution.

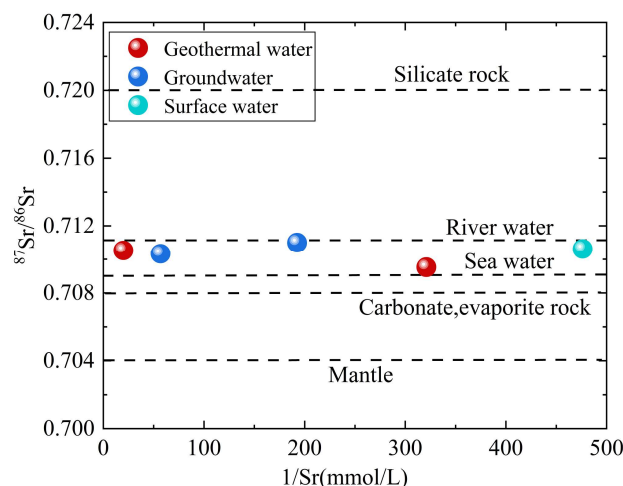


Figure 6. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ for geothermal, ground, and surface water samples from the study area.

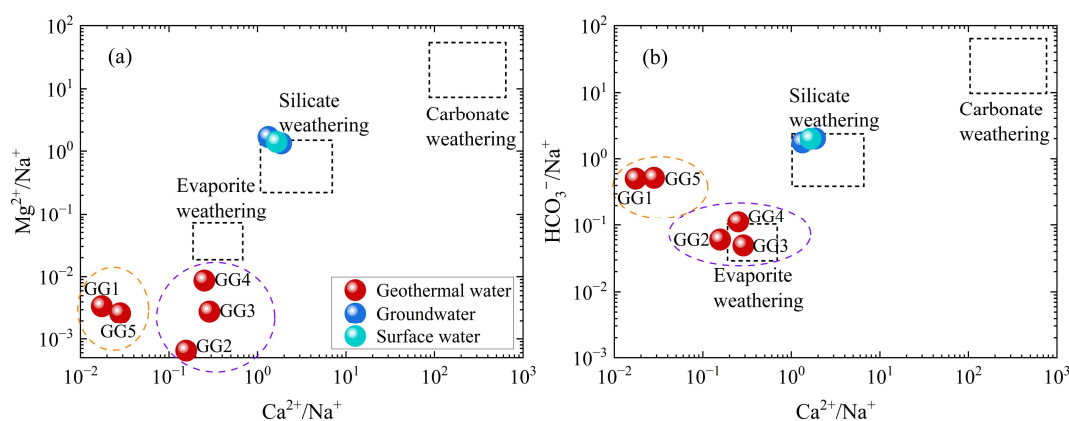


Figure 7. Binary plots of (a) $\text{Ca}^{2+}/\text{Na}^{+}$ versus $\text{Mg}^{2+}/\text{Na}^{+}$ molar ratios and (b) $\text{HCO}_3^{-}/\text{Na}^{+}$ molar ratios, illustrating the dissolution processes controlling hydrochemical composition.

The molar (or equivalent) ratios of major ions have been widely used to understand the geochemical processes that control water chemical composition [30,31]. Surface water and groundwater samples are distributed along the rock salt dissolution line ($\text{Na}/\text{Cl} = 1:1$) and the gypsum and anhydrite dissolution line ($\text{Ca}/\text{SO}_4 = 1:1$) (Figure 8a,c), indicating that the dissolution of rock salt, gypsum, and anhydrite is one of the important sources of ionic components in the surface water and groundwater of the study area. Surface water and groundwater samples are plotted between the $\text{Ca}/\text{HCO}_3 = 1:1$ and $\text{Ca}/\text{HCO}_3 = 1:2$ lines (Figure 8d), suggesting that dissolution of calcite and dolomite constitutes the primary source of Ca^{2+} and HCO_3^{-} in both water types. The relationship between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{HCO}_3^{-} + \text{SO}_4^{2-})$ (Figure 8e) shows that both surface and groundwater samples are distributed along the 1:1 line, confirming that gypsum, anhydrite, calcite, and dolomite are the main sources of ionic components in surface and groundwater. Figure 8f shows that both surface and groundwater samples deviate from the $(\text{Ca} + \text{Mg})/\text{HCO}_3 = 1:1$ line, indicating that dolomite dissolution contributes only minimally to ionic composition in this region and that other hydrogeochemical processes influence the $(\text{Ca} + \text{Mg})/\text{HCO}_3$ ratio.

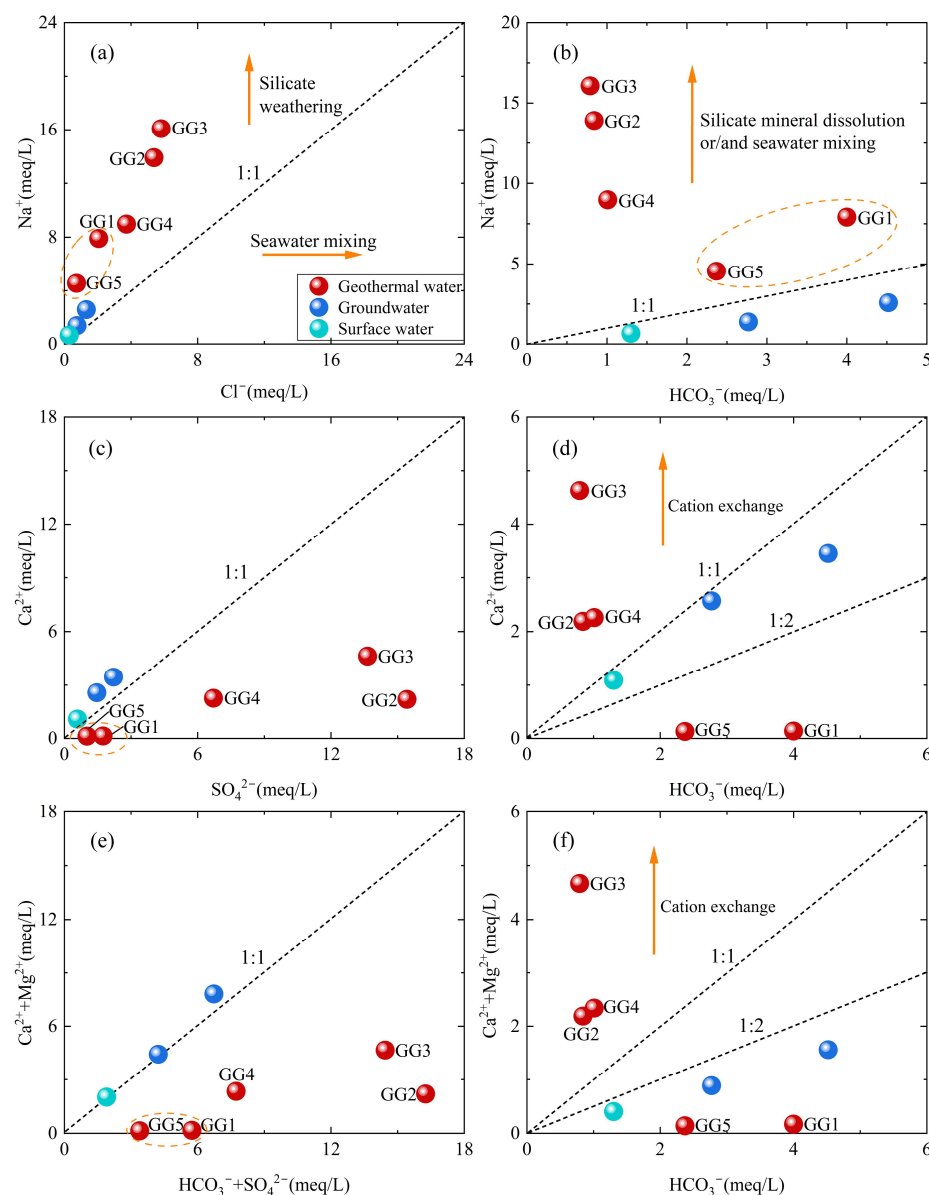
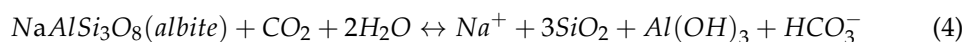


Figure 8. Relationships among major ions in water samples from the study area: (a) Na^+ vs. Cl^- ; (b) Na^+ vs. HCO_3^- ; (c) Ca^{2+} vs. SO_4^{2-} ; (d) Ca^{2+} vs. HCO_3^- ; (e) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. $\text{HCO}_3^- + \text{SO}_4^{2-}$; (f) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^- .

The Na/Cl relationship (Figure 8a) shows that geothermic samples from the study area are plotted above the 1:1 line, indicating that Na^+ is supplied by hydrogeochemical processes that do not contribute Cl^- . The enrichment of Na^+ is primarily due to the dissolution of silicate minerals. The higher SiO_2 content and Na/Cl ratio greater than 1 relative to surface and groundwater suggest that the chemical composition of geothermal waters is influenced by the dissolution of silicates (e.g., albite, Equation (4)). This Na^+ enrichment should not be simply attributed to general plagioclase dissolution, because Ca-rich plagioclase may release relatively more Ca^{2+} during weathering and dissolution. Instead, the elevated Na^+ concentration in geothermal water is more likely controlled by the combined effects of Na-bearing silicate mineral dissolution, such as albite and alkali feldspar dissolution, and cation exchange during water–rock interaction. The Na/ HCO_3^- relationship (Figure 8b) shows that all geothermal water samples from the study area are

plotted above the 1:1 line, further confirming that Na^+ originates from the dissolution of silicate minerals.



The Ca/SO_4 relationship (Figure 8c) shows that geothermal water samples from the study area are all distributed below the 1:1 line, indicating that gypsum dissolution is not the primary source of SO_4^{2-} and that other mechanisms contribute to SO_4^{2-} enrichment. If the SO_4^{2-} in geothermal waters mainly comes from the dissolution of gypsum, its $\delta^{34}\text{S}$ value should be between 10‰ and 28‰; if it mainly comes from the oxidation of sulfides such as stibnite and pyrite in low-temperature hydrothermal ore bodies within the fault zone in the region, its $\delta^{34}\text{S}$ value should be between -4.30 ‰ and -1.32 ‰ [32]. Sulfur isotope data are available only for GG1 and GG2 among the geothermal water samples. The $\delta^{34}\text{S}$ values of GG1 and GG2 are 24.5‰ and 12.8‰, respectively, which fall within the typical range of sulfate derived from gypsum dissolution. Therefore, the sulfur isotope evidence suggests that SO_4^{2-} in GG1 and GG2 is mainly related to gypsum dissolution. However, because $\delta^{34}\text{S}$ data are unavailable for GG3, GG4, and GG5, these samples are not used for sulfur isotope-based source identification of sulfate. The sample points are distributed in the area below the 1:1 line, and the Na^+ content in the geothermal water samples is relatively high. It is likely that cation exchange occurred between the geothermal water and the surrounding rock during runoff. The relatively abundant Ca^{2+} in the geothermal water replaces the Na^+ in the surrounding rock, thereby reducing the Ca^{2+} content and increasing the Na^+ content in the geothermal water. To verify this conclusion, the relationship between the milligram-equivalent concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^-)$ and $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ is used to determine whether cation exchange exists in groundwater. Figure 9a shows that the majority of surface water, groundwater, and geothermal water samples follow a straight line with a slope of -1 , indicating that cation exchange is a significant factor controlling the hydrochemical characteristics of these waters, in addition to the water–rock interaction. To further analyze the strength of cation exchange, a chlor-alkali index diagram is plotted, as shown in Figure 9b. The calculation formulas for both are

$$\text{CAI} - \text{I} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (5)$$

$$\text{CAI} - \text{II} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{HCO}_3^- + \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{NO}_3^-} \quad (6)$$

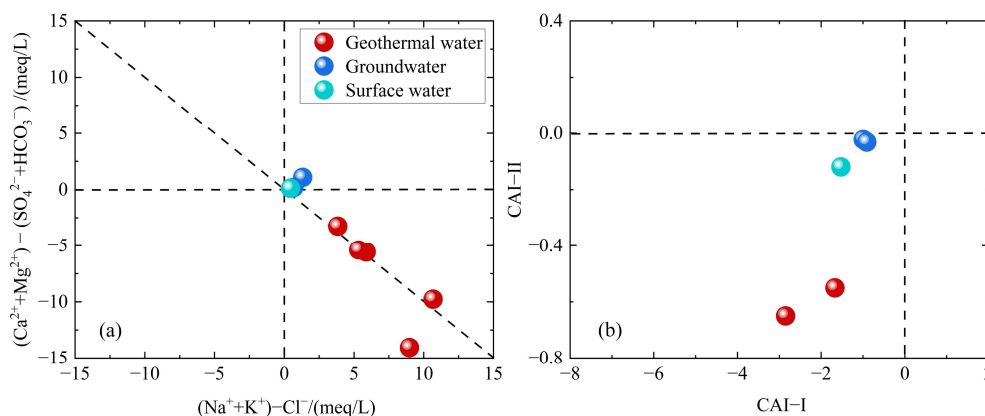


Figure 9. Indicators of cation exchange processes in water samples from the study area: (a) relationship between $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{SO}_4^{2-} + \text{HCO}_3^-)$ and $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$; (b) comparison of CAI-I and CAI-II values.

The ions in Equations (5) and (6) are expressed in equivalent concentrations. If both CAI-I and CAI-II are negative, it indicates that Ca^{2+} and Mg^{2+} in the geothermal water are exchanged for Na^+ and K^+ in the surrounding rock, and the larger the absolute value, the higher the intensity of the ion exchange. Figure 9b shows that both CAI-I and CAI-II of the geothermal water in the study area are negative, indicating the presence of reverse cation exchange, which causes the sample points to deviate from the 1:1 line. Gypsum dissolution is the main source of Ca^{2+} and SO_4^{2-} in the geothermal water; however, due to the consumption of Ca^{2+} by reverse cation exchange, the sample points are distributed below the 1:1 line. The SO_4^{2-} concentrations of GG2, GG3, and GG4 are higher than those of GG1 and GG5, and their $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratios are significantly lower than 1, indicating that cation exchange is stronger in these samples, which is also consistent with the distribution characteristics of Na^+ concentrations in Figure 9a,b.

Figure 8d,f show that all geothermal water samples deviate from the theoretical $\text{Ca}/\text{HCO}_3 = 1:1$, $\text{Ca}/\text{HCO}_3 = 1:2$, $(\text{Ca} + \text{Mg})/\text{HCO}_3 = 1:1$, and $(\text{Ca} + \text{Mg})/\text{HCO}_3 = 1:2$ lines. This deviation suggests that the dissolution of calcite and dolomite is not the primary source of Ca^{2+} , Mg^{2+} , and HCO_3^- in the geothermal waters. Instead, the hydrochemical compositions are likely affected by multiple processes, including deep CO_2 input, silicate mineral dissolution, and cation exchange. GG1 and GG5 are plotted below and to the right of the $\text{Ca}/\text{HCO}_3 = 1:2$ line, indicating relative enrichment of HCO_3^- . This feature is attributed to the upward migration of deep CO_2 along fault zones. CO_2 released from the crust and/or mantle enters the geothermal waters, where it reacts with water to form carbonic acid and subsequently dissociates into HCO_3^- , thereby increasing the HCO_3^- concentration in the water (Equations (7) and (8)). By contrast, GG2, GG3, and GG4 are plotted above and to the left of the $\text{Ca}/\text{HCO}_3 = 1:1$ line, indicating relative enrichment of Ca^{2+} . Combined with the previously obtained chloro-alkaline index results, the negative CAI-I and CAI-II values indicate that reverse cation exchange occurs in the geothermal system. During this process, Ca^{2+} and Mg^{2+} in the geothermal waters are exchanged with Na^+ and K^+ in the surrounding rocks, leading to Na^+ enrichment and causing the samples to deviate from the carbonate dissolution control lines.



In Figure 8e, all geothermal water samples are plotted below the 1:1 line between $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{HCO}_3^- + \text{SO}_4^{2-})$, suggesting an excess of $\text{HCO}_3^- + \text{SO}_4^{2-}$ relative to $\text{Ca}^{2+} + \text{Mg}^{2+}$. In addition to mineral dissolution in shallow aquifers, the excess $\text{HCO}_3^- + \text{SO}_4^{2-}$ is probably supplied by deeper fluids. Meanwhile, Na^+ released from silicate mineral dissolution is required to maintain the charge balance between cations and anions [33]. The higher $\text{HCO}_3^- + \text{SO}_4^{2-}$ concentrations in GG2, GG3, and GG4, together with their elevated Na^+ contents, further indicate that stronger deep water–rock interaction and silicate mineral dissolution occur in these samples.

GG1 and GG5 show similar distribution patterns in Figures 8 and 9 and can therefore be classified as the same type of geothermal water. These samples are characterized by relative HCO_3^- enrichment and low Ca^{2+} and Mg^{2+} concentrations, indicating that their hydrochemical compositions are mainly controlled by deep CO_2 input, with relatively weak water–rock interaction. After entering the geothermal waters along fault zones, deep CO_2 reacts with water to form carbonic acid, which further dissociates into HCO_3^- , leading to HCO_3^- enrichment. In contrast, GG2, GG3, and GG4 have relatively high Na^+ and SO_4^{2-} concentrations, and their $\text{HCO}_3^- + \text{SO}_4^{2-}$ and Na^+ contents increase synchronously. This indicates that these geothermal waters undergo deeper and more intensive water–rock

interaction. The elevated Na^+ contents suggest that silicate mineral dissolution contributes significantly to their hydrochemical compositions. Meanwhile, the available chloro-alkaline index results also indicate the occurrence of reverse cation exchange in the study area, which further affects the distribution of Ca^{2+} , Mg^{2+} , and Na^+ . Overall, the geothermal waters in the study area can be divided into two groups. GG1 and GG5 represent HCO_3^- -enriched geothermal waters mainly controlled by deep CO_2 input, with a relatively low degree of hydrochemical evolution. GG2, GG3, and GG4 represent Na-SO_4 -enriched geothermal waters mainly controlled by deep water–rock interaction and silicate mineral dissolution, with a higher degree of hydrochemical evolution.

Chlorine and bromine are both halogen elements with similar physical and chemical properties. They coexist in seawater, but the content of bromine in freshwater bodies is very low. Therefore, the chlorine–bromine coefficient is the characteristic coefficient of seawater, which can be used to determine the origin of geothermal water and the enrichment of bromine in thermal reservoirs [34]. In modern oceans, the chlorine–bromine coefficient is about 300 (standard value of atmospheric precipitation); in marine sedimentary water (ancient sealed water), the chlorine–bromine coefficient is less than 300; in marine saline sedimentary karst filtration water, the chlorine–bromine coefficient is greater than 300. As can be seen from Figure 10, the chlorine–bromine coefficient of geothermal fluids is greater than 300, suggesting that the geothermal fluids in the study area are filtration water flowing through bromine-poor rocks, belonging to marine saline sedimentary karst filtration water, and the geothermal water in the study area is not affected by seawater intrusion.

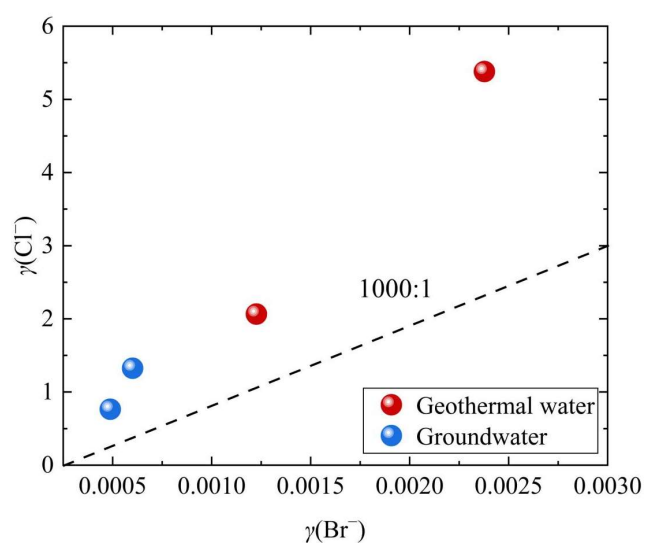


Figure 10. Br^-/Cl^- ratios of geothermal water samples from the study area, indicating bromine enrichment characteristics.

5.3. Reservoir Temperature

5.3.1. Determination of Water–Rock Mineral Equilibrium

Mixing is a common phenomenon in geothermal systems. As underground hot water rises from deep underground to the surface, it may interact with the surrounding rocks and mix with cold water at various depths, causing some minerals in the geothermal temperature scale to be in an unbalanced state with the minerals in the underground hot water, resulting in deviations in the results. Therefore, before selecting a suitable geothermal temperature scale, it is necessary to verify the equilibrium state of the underground hot water and deep minerals [35].

The Na–K–Mg triangle diagram (Figure 11) can be used to analyze the water–rock equilibrium state and determine whether the geothermal water is immature water, partially

mature, or mature water [36]. The Na-K-Mg triangle diagram shows that the geothermal water is located in the partially mature water area. Located in the partially mature water area, it indicates that the geothermal water has not completely reacted with the minerals, the water–rock reaction is low, and it is geothermal circulation water that is greatly affected by shallow groundwater [37]. Both surface water and groundwater are immature water.

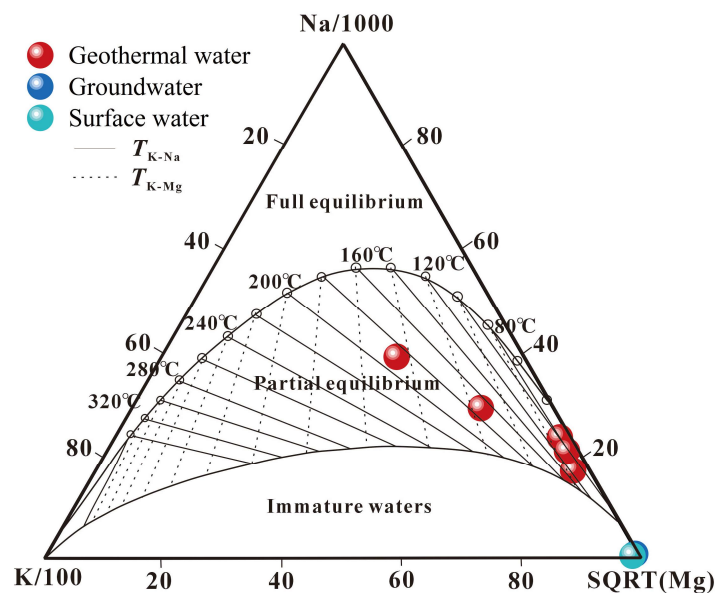


Figure 11. Na/1000–K/100–SQRT(Mg) ternary diagram illustrating the water–rock equilibrium conditions of geothermal waters in the study area.

5.3.2. Multi-Mineral Balancer Method

For subsurface thermal waters that have not reached complete chemical equilibrium, the multi-mineral equilibrium method can be applied to estimate reservoir temperatures. The saturation index (SI) derived from thermodynamic mineral equilibria is useful for analyzing high-temperature water–rock interaction processes, determining whether the aqueous and mineral phases are in equilibrium, and identifying the prevailing dissolution or precipitation conditions [33,38]. When the saturation index of multiple minerals in the geothermal fluid approaches the equilibrium state at a certain temperature ($SI = 0$), this temperature can be considered to be the corresponding deep thermal reservoir temperature. The saturation index SI is a parameter used to judge the degree of mineral saturation. If $SI = 0$, it means that the mineral is saturated; $SI > 0$ means that the mineral is oversaturated and has a tendency to precipitate; $SI < 0$ means that the mineral is unsaturated and will continue to dissolve. In actual calculations, it is generally considered that the SI is in the range of ± 0.5 and is in equilibrium.

The SI calculation results of eight minerals (anhydrite, aragonite, calcite, chalcedony, dolomite, fluorite, gypsum, and quartz) in five geothermal water samples (Table 3) show that the SI of sulfate minerals (anhydrite, gypsum) and dolomite in all samples is < 0 , indicating that the minerals are in an unsaturated state and continue to dissolve. The SI of carbonate minerals (aragonite, calcite) and halide minerals (fluorite) in most geothermal water samples is < 0 , suggesting that the minerals are in an unsaturated state and continue to dissolve. The SI of silicon-containing minerals (quartz, chalcedony) in most samples is between -0.5 and 0.5 , indicating that these minerals are close to a saturated equilibrium state. These results indicate that during the process of deep hot water migrating upward to the surface, it may be mixed with cold water and then rapidly discharged to the surface, retaining the original silicon content [39].

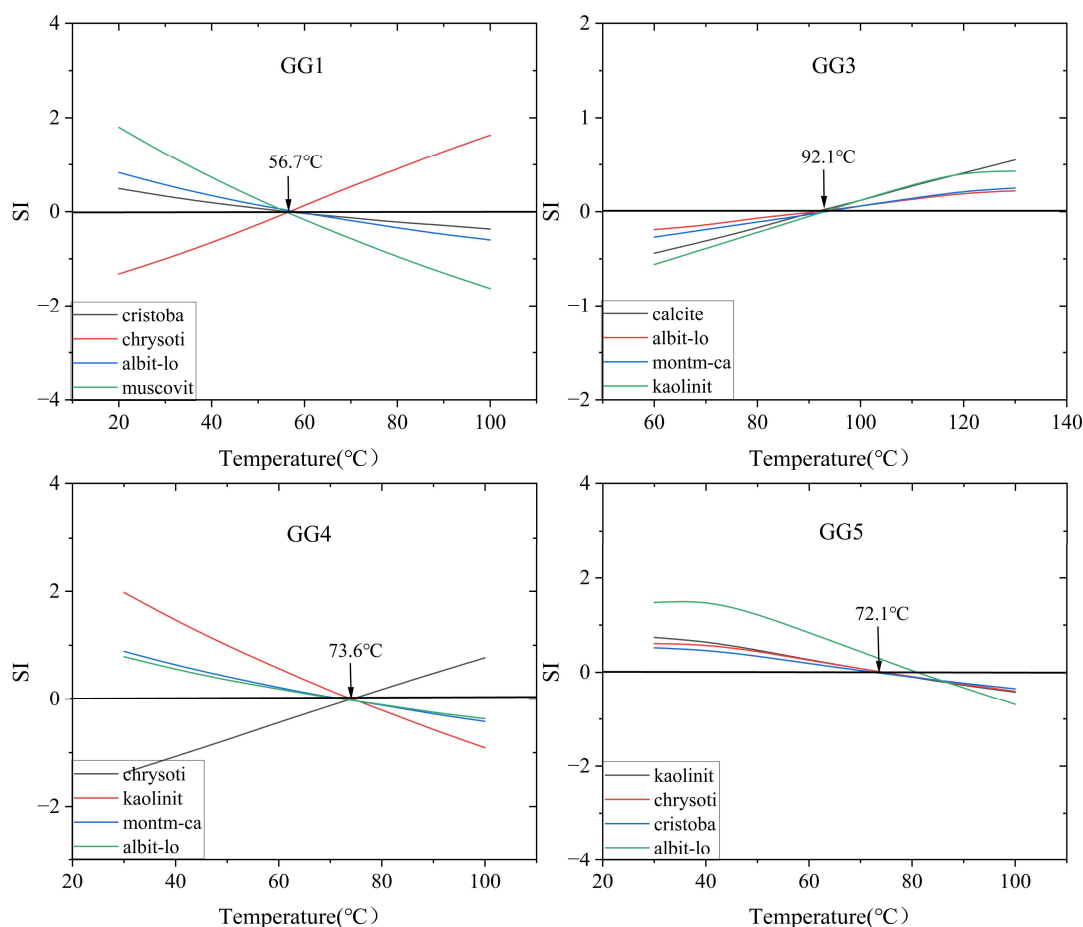
Table 3. Saturation index (SI) values of collected samples.

Sample ID	Anhydrite	Aragonite	Calcite	Chalcedony	Dolomite	Fluorite	Gypsum	Quartz
GG1	−3.10	−0.82	−0.69	0.01	−1.86	−1.54	−2.93	0.41
GG2	−1.37	−3.10	−2.96	0.58	−8.22	0.10	−1.15	1.01
GG3	−0.67	0.43	0.54	0.32	−0.88	0.19	−0.84	0.62
GG4	−1.50	—	—	0.02	—	−0.01	−1.34	0.41
GG5	−3.24	−1.05	−0.92	−0.11	−2.62	−1.23	−3.10	0.27

Note: — denotes that the value is not calculated because CO_3^{2-} data are not available.

The multi-mineral equilibrium diagram method is used to calculate and plot the relationship between the multi-mineral saturation index and temperature to estimate the approximate range of the heat reservoir temperature in the study area. If there are many minerals that are close to equilibrium at a certain temperature (i.e., $\text{SI} = 0$), then this temperature can be used as the heat reservoir temperature [38,40]. This study uses the GeoT program based on an integrated multi-component solute thermometer to estimate the heat reservoir temperature [41]. The program uses the SOLTHERM.H06 thermodynamic database to calculate the ion activity product (Q), thermodynamic equilibrium constant (K), and saturation index (SI) values. It can also optimize the model based on parameters such as concentration/dilution coefficient (cfact) and vapor loss fraction (stwf) to determine the degree of degassing or cold-water mixing during the fluid ascent [42].

The reservoir temperatures estimated from the multi-mineral equilibrium geothermometry diagrams (Figure 12) for samples GG1, GG3, GG4, and GG5 are 56.7 °C, 92.1 °C, 73.6 °C, and 72.1 °C, respectively.

**Figure 12.** Multi-mineral equilibrium geothermometry diagrams employed to estimate reservoir temperatures of geothermal water samples in the study area.

5.3.3. Classical Geochemical Temperature Scale Method

Geochemical temperature scales are often used to estimate the thermal reservoir temperature of deep geothermal fluids [25]. Common geochemical temperature scales include the cation temperature scale and the silica temperature scale [40,43]. The cation temperature scale is applicable to groundwater in which the water–rock reaction has reached equilibrium. The water samples in the study area are partially in equilibrium, so the cation temperature scale is not used for calculations.

The silica temperature scale method means that in geothermal systems, temperature is the main controlling factor affecting the solubility of silica, and the solubility of silica in groundwater increases with increasing temperature. Other factors, such as pressure, humidity, and salinity, have little effect on the solubility of quartz and amorphous silicon under medium- and low-temperature conditions [44]. Therefore, the thermal reservoir temperature can be estimated by measuring the silica concentration in geothermal water. For example, quartz and chalcedony, which are common silica minerals, can be used as geothermal thermometers to estimate the thermal reservoir temperature [45] (Table 4).

Table 4. Commonly used cation and silica geothermometers.

Geothermometer Type	Formula	Author
Quartz (no steam loss)	$T = \frac{1309}{5.19 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)
Quartz (maximum steam loss)	$T = \frac{1522}{5.75 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)
Chalcedony	$T = \frac{1032}{4.69 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)
α -quartz	$T = \frac{1000}{4.78 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)
β -quartz	$T = \frac{781}{4.51 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)
Amorphous silicon	$T = \frac{731}{4.52 - \lg \text{SiO}_2} - 273.15$	Fournier (1977)

The SiO_2 content in geothermal water is often controlled by quartz, chalcedony, and amorphous silica. Figure 13 shows that the sample points fall near the dissolution lines of quartz and chalcedony, with four sample points closer to the SiO_2 dissolution line of quartz. This indicates that quartz and chalcedony control the SiO_2 content in geothermal water, with quartz being the primary factor and chalcedony playing a secondary role. Therefore, this study uses the SiO_2 geothermal temperature scale to estimate geothermal reservoir temperatures.

The reservoir temperatures calculated using the silica geochemical temperature scale are shown in Table 5. However, for medium-temperature and low-temperature geothermal systems, the multi-mineral equilibrium diagram method is generally more accurate and reliable than the single silica temperature scale. The reservoir temperatures calculated by the multi-mineral equilibrium diagram method are close to or higher than those calculated by the silica geochemical temperature scale, mainly because the silica temperature scale is more susceptible to interference from the “cooling process” and thus underestimates the temperature. However, the reservoir temperature calculated by the GG3 multi-mineral equilibrium diagram method is lower than that calculated by the silica geochemical temperature scale, possibly because the geothermal fluid undergoes violent boiling during ascent, and water is lost in the form of vapor, leading to the concentration of dissolved silica in the liquid phase and a relatively higher concentration. Therefore, the reservoir temperature calculated by the multi-mineral equilibrium diagram method is ultimately chosen.

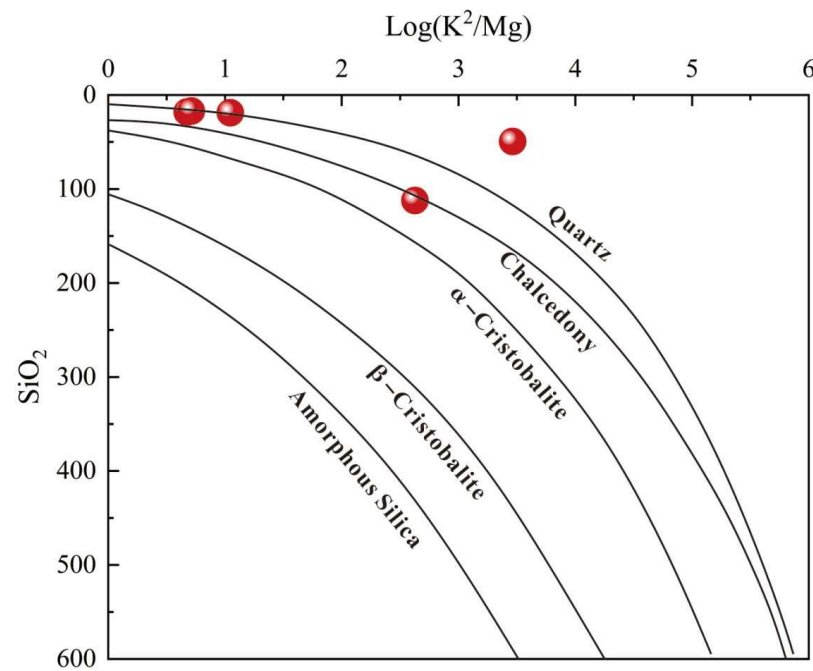


Figure 13. SiO₂ concentration versus log (K²/Mg) diagram of geothermal water samples from the study area.

Table 5. Reservoir temperature estimates obtained from silica geothermometers (°C).

Sample ID	GG1	GG2	GG3	GG4	GG5
Quartz (no steam loss) (°C)	59.53	101.16	143.68	61.31	57.31
Quartz (maximum steam loss) (°C)	65.47	102.00	138.16	67.06	63.49
Chalcedony (°C)	27.31	71.19	117.70	29.16	25.02
α-quartz (°C)	10.56	50.78	93.10	12.26	8.45
β-quartz (°C)	−33.19	4.09	44.28	−31.64	−35.12
Amorphous silicon (°C)	−49.24	−14.58	22.75	−47.79	−51.03

5.4. Circulation Depth and Cold-Water Mixing Ratio

5.4.1. Circulation Depth

Groundwater is often replenished by atmospheric precipitation infiltration and heated by deep heat sources during the deep circulation process. Therefore, the circulation depth of hot water can be roughly calculated using the temperature value of the groundwater heat reservoir in the study area [46]. The calculation formula is

$$H = (T - T_0)/g + h \quad (9)$$

where H is the geothermal water circulation depth (m); T is the reservoir temperature (°C); T₀ is the multi-year average temperature of the study area, taken as 15 °C; h is the depth of the normothermic layer, taken as 20 m; and g is the geothermal gradient. The geothermal gradients for GG1 and GG5 are 2.5 °C/100 m, and for GG2, GG3, and GG4, 3.6 °C/100 m [18]. Calculations show that the geothermal water circulation depth in the study area ranges from 1648 to 2304 m, with an average of 1983 m (Table 6). This depth indicates fault-controlled circulation at moderate depth.

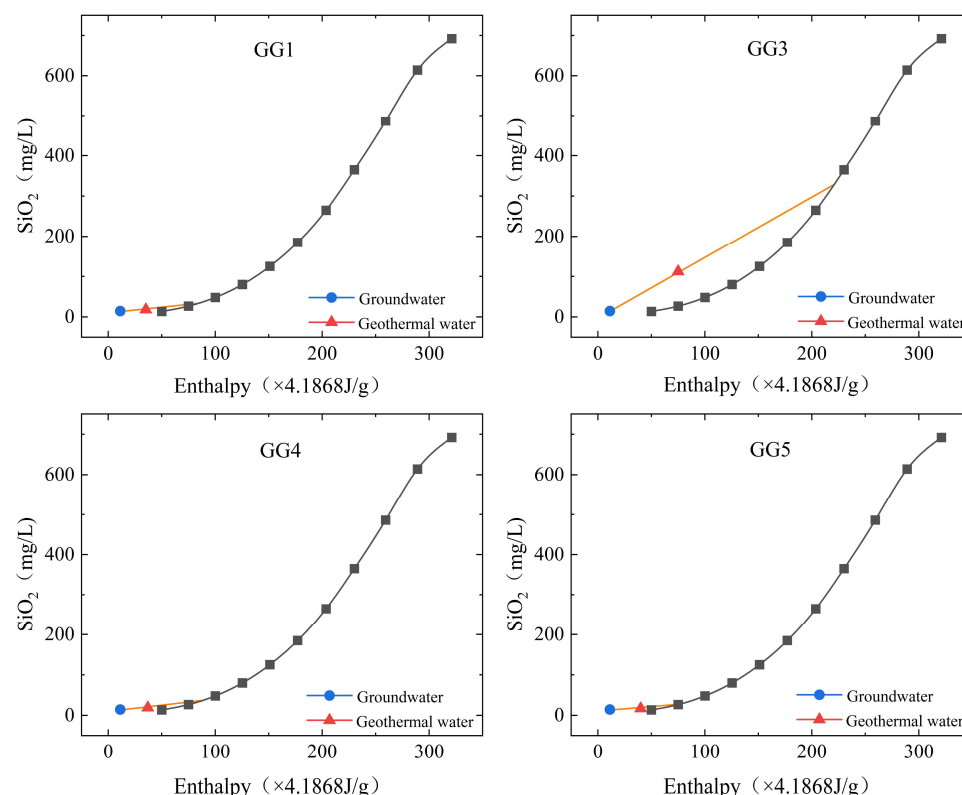
Table 6. Cold-water mixing proportions, circulation depths, and recharge elevations of geothermal waters in the study area.

Sample ID	Recharge Elevation (m)	Circulation Depth (m)	Cold-Water Mixing Ratio
GG1	822	1688	58%
GG2	1274	2114	—
GG3	n.c.	2162	69%
GG4	n.c.	1648	63%
GG5	n.c.	2304	48%

Note: n.c. indicates not calculated. Recharge elevations are corrected only for GG1 and GG2 because original sampling elevations are unavailable for the literature-derived samples GG3, GG4, and GG5.

5.4.2. Cold-Water Mixing Ratio

The silicon–enthalpy model diagram can be used to estimate the cold-water mixing ratio in geothermal water [38]. Underground hot water may mix with shallow cold water during its ascent. The mixing of deep geothermal water and shallow cold water can be described by the relationship between enthalpy (heat content) and SiO_2 concentration. According to Figure 14, the cold-water mixing ratios of the GG1, GG3, GG4, and GG5 geothermal wells are estimated to be 58%, 69%, 63%, and 48%, respectively. The geothermal wells in the study area generally exhibit relatively high cold-water mixing ratios, which are consistent with the fault development characteristics of this region.

**Figure 14.** Silicon–enthalpy model curves illustrating cold–hot water mixing under quartz dissolution equilibrium in the study area.

5.5. Formation Models of Underground Hot Water

Based on the geological structure, hydrogeochemistry, and isotopic characteristics of the study area, the genesis and cyclic evolution of the geothermal waters are analyzed (Figure 15). The geothermal waters are mainly recharged by atmospheric precipitation and migrate downward along fault fracture zones under gravity. During fault-controlled

circulation at moderate depth, groundwater is heated mainly by the regional geothermal gradient and crustal heat flow. The circulation depths of the geothermal waters range from 1648 to 2304 m, and the reservoir temperatures range from 56.7 to 92.1 °C.

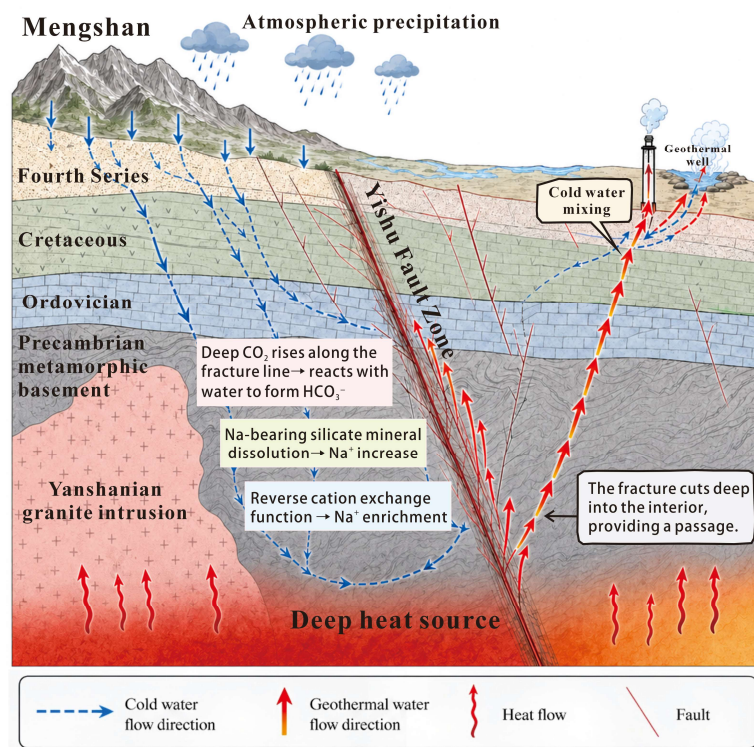


Figure 15. Conceptual model illustrating the geothermal water circulation process in the study area.

During circulation, the geothermal waters undergo different degrees of water–rock interaction and can be divided into two hydrochemical groups. GG1 and GG5 are characterized by HCO_3^- enrichment and relatively low Ca^{2+} and Mg^{2+} concentrations, indicating that their hydrochemical compositions are mainly controlled by deep CO_2 input, with relatively weak water–rock interaction. Deep CO_2 migrates upward along fault zones, reacts with water to form carbonic acid, and subsequently dissociates into HCO_3^- , thereby forming HCO_3^- –Na type geothermal waters. In contrast, GG2, GG3, and GG4 show higher Na^+ and SO_4^{2-} concentrations, as well as higher $\text{HCO}_3^- + \text{SO}_4^{2-}$ contents, suggesting more intensive deep water–rock interaction and a higher degree of hydrochemical evolution. In these samples, Na-bearing silicate dissolution releases abundant Na^+ , whereas SO_4^{2-} enrichment may be related to sulfate mineral dissolution and/or deep fluid input. Cation exchange further modifies the distribution of Na^+ , Ca^{2+} , and Mg^{2+} , promoting the formation of SO_4 –Na and $\text{Cl}\cdot\text{SO}_4$ –Na type geothermal waters. Driven by hydraulic gradients and thermal forces, the geothermal waters then migrate toward lower elevations and mix with shallow cold water during ascent, with estimated cold-water mixing ratios of 48–69%. Finally, the mixed geothermal waters ascend and discharge along shallow fracture channels.

6. Conclusions

The YSFZ is a typical major deep-seated fault zone in eastern China, which is situated at the tectonic junction of the North China Craton and the Yangtze Craton. Abundant geothermal resources are distributed along this fault zone, making it a key area for geothermal resource exploration and research in eastern China. To elucidate the genetic mechanism of geothermal resources in the middle segment of the YSFZ, eight samples were collected

in this study. By adopting hydrogeochemical and isotopic analysis methods, a detailed investigation is conducted on the chemical types of groundwater, water–rock interactions, and circulation processes in the study area. The results show that:

- (1) Significant differences exist in the major and trace elements among geothermal water, groundwater and surface water in the study area. Geothermal water exhibits higher concentrations of Na^+ , SO_4^{2-} and Cl^- , indicating that it has experienced water–rock interaction during deep circulation and runoff processes. The hydrochemical types of geothermal water are mainly characterized by the $\text{HCO}_3\text{--Na}$ and $\text{Cl}\cdot\text{SO}_4\text{--Na}$, while surface water is dominated by the $\text{HCO}_3\cdot\text{SO}_4\text{--Na}\cdot\text{Ca}\cdot\text{Mg}$ type. Groundwater is characterized by $\text{HCO}_3\cdot\text{SO}_4\text{--Na}\cdot\text{Ca}\cdot\text{Mg}$ and $\text{HCO}_3\cdot\text{SO}_4\text{--Ca}\cdot\text{Mg}$.
- (2) The analysis of δD and $\delta^{18}\text{O}$ indicates that the geothermal water is predominantly recharged by atmospheric precipitation at elevations ranging from 822 m to 1274 m. In light of regional geological and hydrogeological conditions, the recharge area has been tentatively identified as Mengshan Mountain and its adjacent mountainous regions. The main solute molar ratio, $^{87}\text{Sr}/^{86}\text{Sr}$ isotope and $\delta^{34}\text{S}$ isotope composition indicate that the hydrochemical characteristics of geothermal water, surface water and groundwater in the study area are mainly controlled by water–rock interaction, showing mixed geochemical characteristics of silicate and evaporite mineral dissolution.
- (3) The geothermal waters can be further divided into two groups: GG1 and GG5 are mainly controlled by deep CO_2 input and show relatively weak hydrochemical evolution, whereas GG2, GG3, and GG4 are mainly affected by deeper water–rock interaction, silicate mineral dissolution, and reverse cation exchange, showing a higher degree of hydrochemical evolution.
- (4) Geothermal water circulates at a depth of 1648~2304 m. During fault-controlled circulation, geothermal water is heated mainly by the regional geothermal gradient and crustal heat flow. The reservoir temperature calculated by the multi-mineral equilibrium diagram method is 56.7~92.1 °C. In the process of rising to the surface, the groundwater is mixed with cold water to varying degrees. The cold-water mixing ratio is 48%~69%, which is relatively high and consistent with the fault development characteristics of the area.

Author Contributions: Conceptualization, X.Y., S.Z. (Shouchuan Zhang) and K.L.; methodology, X.Y. and S.Z. (Shuhui Zheng); software, X.Y.; validation, S.Z. (Shouchuan Zhang), K.L. and S.Z. (Shuhui Zheng); formal analysis, X.Y.; investigation, X.Y., Y.Z. and L.W.; resources, S.Z. (Shouchuan Zhang), K.L. and S.Z. (Shuhui Zheng); data curation, X.Y. and Y.Z.; writing—original draft preparation, X.Y.; writing—review and editing, S.Z. (Shouchuan Zhang), K.L., S.Z. (Shuhui Zheng), Y.Z., L.W., G.B. and J.W.; visualization, X.Y., G.B. and J.W.; supervision, S.Z. (Shouchuan Zhang) and K.L.; project administration, S.Z. (Shouchuan Zhang) and K.L.; funding acquisition, S.Z. (Shouchuan Zhang) and K.L. All authors have read and agreed to the published version of the manuscript.

Funding: This study is supported by the Deep Earth Probe and Mineral Resources Exploration—National Science and Technology Major Project (2024ZD1004103), the Chinese Academy of Geological Sciences Basal Research Fund (No. JKYZD202401 and No. JKY202406), the Open Foundation of the Key Laboratory of Coupling Process and Effect of Natural Resources Elements (No. 2024KFKT001), the Qinghai Provincial Key Laboratory of Geology and Environment of Salt Lakes (No. 2024-KFKT-B10), and the Open Research Fund Project of Hebei Key Laboratory of Geological Resources and Environment Monitoring and Protection (No. JCYKT202404).

Data Availability Statement: The original contributions presented in this study are included in the article material. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: Author Shuhui Zheng was employed by Shandong Surveying and Design Institute of Water Resources Co., Ltd. The remaining authors declare that the research was conducted

in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

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